


EP 31757 (2)

204114-06255
B6C8
**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B32B 9/00, 9/04, 13/04, 15/04, 19/00, C01B 31/00, 31/02, C23C 16/00, F01L 1/44, 3/00, 3/04, F02B 75/08, 77/02	A1	(11) International Publication Number: WO 97/14555 (43) International Publication Date: 24 April 1997 (24.04.97)
(21) International Application Number: PCT/US96/15367 (22) International Filing Date: 25 September 1996 (25.09.96) (30) Priority Data: 08/538,472 3 October 1995 (03.10.95) US (71) Applicant: ADVANCED REFRACTORY TECHNOLOGIES, INC. [US/US]; 699 Hertel Avenue, Buffalo, NY 14207 (US). (72) Inventors: GOEL, Arvind; 156 Highgate Avenue, Buffalo, NY 14214 (US). BRAY, Donald, J.; 257 Sausalito Drive, East Amherst, NY 14051 (US). (74) Agents: WEYAND, Karla, M. et al.; Nixon, Hargave, Devans & Doyle L.L.P., Clinton Square, P.O. Box 1051, Rochester, NY 14603 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: DIAMOND-LIKE NANOCOMPOSITE THIN FILMS FOR AUTOMOTIVE POWERTRAIN COMPONENT COATINGS (57) Abstract A method for inhibiting wear and reducing friction of components in a powertrain assembly comprising applying to said component a coating made from a class of diamond-like solid state materials formed interpenetrating networks comprising a first network of diamond-like carbon stabilized by hydrogen, a silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

**DIAMOND-LIKE NANOCOMPOSITE THIN FILMS
FOR AUTOMOTIVE POWERTRAIN COMPONENT COATINGS**

5 **FIELD OF THE INVENTION**

 The present invention relates generally to low friction diamond-like nanocomposite coatings comprising an amorphous matrix. More particularly, the present invention relates to low friction diamond-like
5 nanocomposite compounds for use as friction reducing protective coatings on automotive powertrain assemblies.

10 **BACKGROUND OF THE INVENTION**

 Internal combustion engines provide a harsh environment for the component parts, especially the parts which move. Components of the powertrain assembly in most internal combustion engines often move at high
15 speeds and in close proximity to interacting surfaces. Such components must be machined and manufactured to specific tolerances that enable operating at high temperatures and low temperatures, without risking material stress, fatigue and/or failure. The components
20 may or may not operate in the presence of lubricant. However, the considerations of noise, vibration, and wear relative to frictional forces generated between interacting surfaces over prolonged periods at high operating temperatures remain.

25 Internal combustion engines were once made from heavier metals which were known to be durable and perform well under harsh temperature and frictional conditions. However, to achieve more cost-efficient and fuel-
30 efficient vehicles, today's engines and powertrain assemblies require lighter components. Unfortunately, the lightweight metals of choice, such as aluminum and

- 2 -

aluminum alloys, are not as durable as their stronger, heavier predecessors. In addition, while aluminum pistons and bores (cylinders) are desirable from a cost and machining standpoint, the aluminum/aluminum interface of the bores, pistons, valves, etc. does not work if there is not sufficient lubrication. This is a problem for "cold starts", where the engine and parts must cycle briefly without adequate lubrication (i.e. before lubricant is pumped to the site). As a result, cast iron liners, coatings or platings have been used in the aluminum bores to achieve the proper compatibility of the components during cold starts. In addition to the higher costs, the cast iron liners are heavy and must have a thermal expansion factor taken into account since the cast iron and aluminum have varying expansion coefficients over the operating temperature range of from about -100°C to about 350°C.

While cast iron plating may provide a workable solution, the plating process produces an undesirable amount of hazardous cyanide waste which is expensive to properly dispose of. It would be desirable to coat the aluminum and aluminum alloy components with a sufficiently strong and lubricious coating to facilitate the use of an all aluminum containing powertrain assembly and engine.

The application of hard and lubricious thin films, or coatings, formed from a combination of amorphous carbon-hydrogen-silicon to a substrate are known. However the film deposition conditions often require heating in a vacuum at 600°C. Heating at such temperature restricts the types of substrates which may be coated with such a coating, since the substrates could melt, lose original shape, or otherwise fatigue.

- 3 -

The use of deposition techniques such as radio frequency (RF), ion beam and microwave plasma chemical vapor deposition (CVD) and physical vapor deposition (PVD) to deposit hard, lubricious coatings on substrates is known. However, delamination and non-adherence conditions pose problems for such coatings. Thicker deposited layers would seem to provide greater wear resistance and protection to the coated substrate. However, as thickness of the deposited coating layer increases, the likelihood of delamination of the coating also increases due to high internal stresses common in these coatings. A successful coating must have superior adherence, to a degree yet unknown to most hard coatings.

U.S. Patent No. 5,249,554 discloses a hard, wear-resistant coating system comprising a film and an interlayer which adheres to powertrain components resulting in reduced friction and wear. The films are deposited by physical or chemical vapor deposition of coating systems of various combinations of amorphous hydrogenated carbon, silicon-doped amorphous hydrogenated carbon, boron-, nitrogen-, boron nitride-, or metal- and doped amorphous hydrogenated carbon, silicon, silicon carbide, silicon nitride, boron nitride, and mixtures thereof. However, the coatings require the use of an interlayer. The disclosed interlayer mitigates the chemical incompatibility of certain coatings with certain substrates.

Coating systems having such additional layers, or interlayers, have many potential shortcomings. Depositing a required interlayer increases coating system complexity and cost. Further, interlayers themselves run the risk of delamination over time. Still further, such interlayers must be chemically compatible with both the substrate and the coating or outer film layer, thus increasing the complexity of factors taken into

- 4 -

consideration for a particular coating process, and limiting the number of possible substrate/interlayer coating combinations.

5 Diamond-like coatings (DLCs) have been proposed for uses where wear-resistance is desired. However, most known DLCs will not adequately adhere to metals without additional compatibilizing interlayers, especially when the metal substrate to be coated must operate over a
10 widely varying temperature range during its useful life. DLCs therefore continue to have thermal stability problems.

A hard, wear-resistant and lubricious coating
15 which could be applied in thin layers directly to substrates, especially substrates used as components for powertrain assemblies, without the need for additional compatibilizing layers or interlayers would be extremely useful and desirable.

20

SUMMARY OF THE INVENTION

The present invention relates to coated
25 powertrain components in internal combustion engines. The powertrain component comprises a substrate made from a metal-containing or non-metal containing materials. The substrate is coated with a wear-resistant and friction reducing coating. The coating is made from a
30 class of diamond-like solid state materials formed from interpenetrating networks comprising a first network of diamond-like carbon stabilized by hydrogen, a silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds
35 containing elements from Groups 1-7b and 8 of the periodic table.

- 5 -

In a further embodiment of the present invention, an internal combustion engine is disclosed comprising a powertrain component. The powertrain component comprises a substrate made from a metal-
5 containing or non-metal containing materials. The substrate is coated with a wear-resistant and friction reducing coating. The coating is made from a diamond-like atomic scale material formed from interpenetrating networks comprising a first network of diamond-like
10 carbon stabilized by hydrogen, a silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

15 In a still further embodiment of the present invention, a method for inhibiting wear of a component in a powertrain assembly is disclosed. A powertrain component is provided and coated with a coating made from a diamond-like material formed from interpenetrating
20 networks comprising a first network of diamond-like carbon stabilized by hydrogen, a second silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

25 In another embodiment of the present invention, a method for reducing friction of a powertrain component in a powertrain assembly is disclosed. At least one of two adjacent powertrain components are provided and
30 coated with a coating with made from a diamond-like material formed from interpenetrating networks comprising a first network of diamond-like carbon stabilized by hydrogen, a second silicon network stabilized by oxygen, and optionally at least one network made from dopant
35 elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

- 6 -

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the principle microstructure of two-network (A), intermediate (B), and three-network (C) nanocomposites.

FIG. 2 is a schematic diagram detailing the main method of fabrication of the DLN coatings.

FIG. 3 is a schematic diagram detailing the methods of fabrication of DLN coatings using reflected beam flow.

FIG. 4 is a schematic diagram detailing a preferred DLN fabrication and deposition chamber.

FIG. 5 is a graph of DLN and DLC hardness values plotted versus compressive stress values.

FIG. 6 is a schematic sectional view of an internal combustion engine showing a valve lifter assembly as illustrative of other power train components.

DETAILED DESCRIPTION OF THE INVENTION

The powertrain coatings of the present invention result in superior wear-resistance of the coated components, which would lead to significant improvements in the manufacture of internal combustion engines. The powertrain components comprise substrates made from metal-containing, ceramic-containing or plastic-containing compounds, or combinations thereof. The substrate is coated with a wear-resistant and friction reducing coating. The coating is made from a class of diamond-like solid state materials formed from interpenetrating networks comprising a first network of

- 7 -

diamond-like carbon stabilized by hydrogen, a second silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

The diamond-like nanocomposite films and coatings (DLNs) used to coat the powertrain components of the present invention find their advantage in their superior hardness, adherence, temperature stability, and overall durability. The DLNs, especially the metal-doped DLNs, combine high microhardness with high elasticity. The microhardness values of the DLNs of the present invention range from about 6 to about 30 GPa, while displaying reduced intrinsic stress, especially as compared to DLCs. See Figure 5.

In addition to the protective and wear-resistant properties of the powertrain component coatings of the present invention, the coatings are strong and erosion resistant, such as to chemicals, erosion, abrasion, or ablation while also being highly thermally stable. The coatings would therefore be impervious to physical or chemical attack, and highly resistant to incident laser or other radiation. The resistance of the coatings of the present invention to erosion, reduces the possibility of, for example, physical chipping. This results in the surface of the substrate also being less likely to environmental corrosive forces. The coatings have excellent adherence to the substrate without applying an interlayer, and are resistant to thermal shock and elevated temperatures beyond those known to erode or graphitize known diamond-like coatings.

The term "powertrain components" encompasses the parts of a machine assembly responsible for generating power leading to work or motion. In an

- 8 -

automotive internal combustion engine, the powertrain assembly comprises the valves, pistons, rings, etc. of the engine block, the gears, linkages, rods and joints, etc. which extend from the engine block to the
5 transmission, the components of the transmission itself, and all linkages extending from the transmission and connecting to the axel assemblies. The powertrain components may include more components as would be readily understood by those skilled in the field of
10 engine and powertrain assemblies. What is important is that at least two parts come into close proximity or contact in such a way, and at such temperatures, that frictional forces can lead to the wear and breakdown of the parts without sufficient lubrication and wear-
15 resistant coatings.

Wear-resistance refers to the ability of a material to resist mass removal in an abrasion/wear environment. The lower the mass removal for a given set
20 of conditions, the higher is the material's wear resistance.

The fundamental structure of the preferred wear-resistant atomic scale diamond-like nanocomposites
25 (DLNs) used to coat the selected substrates is comprised of two or more self-stabilized random networks, each stabilized chemically by additional atomic species, while both networks also structurally stabilize each other. An example of a material with such a structure is the
30 diamond-like nanocomposite (DLN) which is the subject of U.S. Patent No. 5,352,493 and U.S. Serial No. 08/249,167 filed May 24, 1994.

In the DLN, a random carbon network, mainly in
35 the form of sp^3 bonded carbon is chemically stabilized by hydrogen atoms, and a glass-like silicon network is chemically stabilized by oxygen atoms, resulting in a

- 9 -

purely amorphous structure. "Amorphous" as used herein refers to a random structure or arrangement of atoms in a solid state that results in no long range regular ordering, and no crystallinity or granularity. The DLN materials have an amorphous structure and do not contain clusters greater than 10 Angstroms. This absence of clusters at the atomic scale is a key characteristic of the DLN coatings of the present invention. Clusters can destroy amorphous nature of the structure, and can serve as active centers of degradation.

The DLNs of the present invention contain no clusters or ordering greater than that defined by one-third the radius of the coordination sphere. This structure has been confirmed via electron projection methods, scanning tunneling microscopy, atomic force microscopy, glancing x-ray and electron diffraction techniques and high resolution transmission electron microscopy (TEM). Cluster formation is prevented in the sources, in the primary plasma, in the chamber space, and during film growth.

The atomic structure of the class of diamond-like nanocomposite (DLN) solid state materials of the present invention is shown in FIG. 1(A). The materials may have one or more separate disordered networks of dopants, as shown in FIG. 1(B) and 1(C). The dopants may be any one or a combination of the transition metals and non-metals of the Groups 1-7b and 8 of the periodic table, and all three types of networks (C-H; Si-O and the dopant network, Me-Me) bonded to each other predominantly by weak chemical bonds. The network elements other than the C-H network may be referred to as alloying elements. Further, silicon and oxygen atoms may also be used in the dopant networks with other elements and compounds.

- 10 -

The DLN coatings of the present invention may comprise a two component network: the diamond-like carbon-hydrogen network interpenetrated with the glass-like silicon-oxygen network. A three component network may also be used comprising the Si-O and C-H networks with one or more dopant networks, with the dopants being interspersed with the previously mentioned two interpenetrating networks. In this instance three or more interpenetrating networks will be present in the DLN to form a so-called Me-DLN (metal-diamond-like nanocomposite) network. It is understood that non-metal dopant networks, may also be incorporated as the optionally present dopant networks interpenetrating the C-H and Si-O networks.

15

The three networks (C-H matrix, Si-O matrix and a dopant matrix) are bonded to one another mainly by weak chemical bonds. Carbide formation can be prevented even at metal concentrations as high as 50% (verified using Auger electron spectroscopy, electron spectroscopy for chemical analysis (ESCA), extended x-ray absorption fine structure spectroscopy (EXAFS) and Fourier transform infrared spectroscopy (FTIR)). Again, the properties of these materials can be varied over wide ranges depending on the dopant and the concentration selected, as well as the deposition technique and parameters. As already mentioned, the structure of these composites can be tailored at the molecular level. Therefore, unique electrical, optical, and other desirable solid state properties with desired mechanical strength, hardness and chemical resistance can be imparted on the DLN coatings which can be used to coat metal-containing and non-metal containing substrates.

35

Preferred dopant elements to be used in the Me-DLN network, and which are particularly effective for use as dopants in a corrosion-resistant Me-DLN coating are B,

- 11 -

Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Mn, Ni, Ti, Zr, Cr, Re, Hf, Cu, Al, N, Ag and Au; with W, Cr, Zr, Ti and Hf being preferred. Preferred compounds which may be used as dopants include TiN, BN, AlN, ZrN and CrN; with TiN and ZrN being most preferred.

The carbon content in the diamond-like nanocomposite is greater than about 40 atomic % of the DLN preferably about 40 to about 98 atomic %, more preferably about 50 to about 98 atomic %. Although the DLN may theoretically be prepared without any hydrogen, the hydrogen content is preferably at least about 1 atomic % and up to about 40 atomic % of the carbon concentration. The sum of the silicon, oxygen and dopant elements and dopant containing compounds is greater than about 2 atomic % of the DLN. In one preferred embodiment, the ratio of carbon to silicon atoms is from about 2:1 to about 8:1, hydrogen to carbon atoms is about 0.01:1 to about 0.4:1, silicon to oxygen atoms is about 0.5:1 to about 3:1, and dopant to carbon atoms is about 0:1 to about 1.5:1. Therefore, in the DLN network, for every 1 part carbon, there is from about 0.01 to about 0.4 parts hydrogen, from about 0.125 to about 0.5 parts silicon, and from about 0.0375 to about 1.0 parts oxygen. In such a scheme, if a third dopant network were present, for every 1 part carbon, there would be from about 0.01 to about 1.5 parts dopants depending upon the desired characteristics to be imparted to the Me-DLN network.

The low intrinsic stress found in the DLNs contributes to their wear-resistance and low coefficient of friction properties. By contrast, known DLC films typically possess high intrinsic stresses, and as a result usually suffer from pin holes and overall porosity. In addition, intrinsic stress limits the thickness of the DLC layer that can be achieved, as delamination or other adherence problems will often

- 12 -

occur. Due to the comparatively low intrinsic stress present in DLN films and coatings of the present invention, such coatings are pore-free, and therefore resist wear and permeation. As shown in Example 4 and
5 Figure 5, the DLNs of the present invention display both low intrinsic stress and yet high hardness values.

The presence of the glass-like silicon network, stabilized by oxygen, serves to prevent the growth of
10 graphitic carbon at high temperatures, to prevent metal cluster formation in metal-containing three-network nanocomposites, and reduce the internal stress in the nanocomposite structure and thereby enhance the adhesion to substrates. This appears to lead to superior
15 adherence of the DLNs of the present invention to the substrate material. The DLNs adhere well to both metal-containing and non-metal containing substrates including metals, metal alloys, plastics, ceramics and combinations thereof.

20

As already mentioned, to improve the adherence of DLC coatings, an intermediate layer, or interlayer, is required between the substrate and the DLC coating. Often, if the DLC coatings are too thick, delamination
25 occurs due to high internal stress. Surprisingly, with the DLN coatings of the present invention, adherence is so good that an interlayer is not required. As a result, the DLN coating may be applied directly to the substrate, and more thickly without risking delamination from the
30 substrate. The ability to apply a thicker layer of DLN coating results from the low intrinsic stress due to the Si-O network, and is believed to contribute to the superior erosion resistance of the DLN-coated substrates. Of course, should an interlayer be desired for some
35 reason, the DLNs may incorporate interlayers.

- 13 -

The environmental conditions faced by powertrain components are severe and extreme. Some components must face high speed revolutions or linear stroke cycles in excess of 5000 rpm. These moving components, as well as the stationary components contacted by the moving components, are subjected to extreme heat during operation, sometimes followed by periods of extreme cold. Operating temperatures may range from about -100°C during cold engine start up to about 350°C.

The adherence and wear-resistance of the DLN coatings of the present invention may be further assisted by the ability of the DLNs to have their characteristics, properties and performance tuned "tuned", or selectively altered according to the desired application. Such "tuning" is accomplished by incrementally altering the particular dopant as well as the dopant concentration. The DLNs may also have their properties altered when no dopants are included. Such changes in properties in the two-network system can be achieved by altering the deposition conditions in terms of temperature and pressure, etc.

The DLNs of the present invention have temperature stability far exceeding that of traditional diamond-like (DLC) materials. Crystalline diamond is stable to approximately 1100°C, upon which graphitization occurs. Quartz has long term thermal stability to 1470°C, and short term thermal stability up to 1700°C. Traditional, non-alloyed diamond-like (DLC) films are stable only to about 250-600°C before graphitization occurs. By contrast, the DLN structures used to provide the corrosion and erosion resistant coatings of the present invention have long term stability to over 1000°C and short term stability to 2000°C. Therefore the thermal

stability of the DLNs exceeds that of DLCs while preserving the amorphous, diamond-like state.

Further, in the range of from about 600°C to
5 about 1000°C, the chemical bonds of the carbon matrix of
DLN materials partly change from sp^3 to sp^2 . However, the
general structure of the nanocomposite and their
"diamond-like" properties are preserved. By contrast,
under similar conditions, the usual "diamond-like" carbon
10 (DLC) is graphitized and loses its diamond-like
properties. In the range of from 400°C to 500°C
(preferably 430°C), a reverse transition is observed,
whereby the ratio of sp^3 to sp^2 is increased.

15 The density of the C-H and Si-O two network DLN
varies from about 1.8 to about 2.1 g/cm³. The rest of the
space is taken up by a random network of nanopores with
diameters varying from about 0.28 to about 0.35 nm. The
nanopore network does not form clusters or micropores.
20 The properties of the two-network DLN may then be
tailored by adding dopant. The dopants fill the nanopore
network in a random fashion, eventually resulting, at a
certain dopant concentration, in an additional network
without clusters or microcrystalline grains, even at
25 concentrations as high as 50 atomic %. At concentrations
below about 10 atomic %, the dopants are distributed as
separate atoms in the nanopores of the diamond-like
matrix. The average distance between dopant atoms in
this quasi-random structure can be controlled by the
30 concentration of the dopant. When the relative
concentration of the dopant element or compound reaches
about 20-25 atomic %, the dopants form the third (Me-Me)
network in the DLN structure as shown in FIG. 1(C).

35 The electrical properties of the DLN structures
of the present invention can be continuously varied over
a wide magnitude (at least about 20 orders of magnitude)

- 15 -

from a highly dielectric state to a highly conductive state while preserving and improving the properties of the DLN state. A transition to a superconducting state, with the absence of electrical resistivity, is observed at low temperatures for certain three-network nanocomposite networks.

The DLNs may be synthesized via co-deposition by clusterless beams of ions, atoms or radicals of the relevant elements, where the mean free path of each particle species exceeds the distance between its source and the growing particle film surface, and each beam contains particles of well-defined energy. Carbon-containing particle beams can be produced by plasma discharge in a plasmatron and extracted as charged particles by a high-voltage field in a vacuum chamber and directed onto the substrate. At least 50% of the carbon-containing particles have kinetic energy above about 100 eV. The temperature of the substrate during growth should not exceed 500°C.

Figure 2 shows one preferred embodiment of the coating chamber used for the DLN coating deposition process. A vacuum deposition chamber 1 is provided to coat a substrate sample. A precursor inlet system 13, comprises a metal tube and a porous ceramic material 3 through which a liquid precursor, preferably a polysiloxane, is injected. The precursor inlet system 13 is shown incorporated into the chamber through the chamber base plate 11. The thermocathode 2 comprises a resistively heated thoriated tungsten filament 4. Substrates 5 to be coated with DLN film are attached to the substrate holder 6. The power supply 8 is used for biasing the substrates (DC or RF). In practice the system is "pumped down" using normal vacuum pump down procedures. A gate valve (not shown) located on port 7 is closed and the system is backfilled with dry air,

- 16 -

nitrogen or argon until the chamber reaches atmospheric pressure. The door of the chamber, 9, is then opened and substrate to be coated 5 are attached to the substrate holder 6 using any of many possible methods (spring clip, screw, clamp, etc.). Special fixtures may be required for substrates of special shapes. The substrate holder is designed in a way that it will also hold a cylinder sample (not shown), which, in operation, rotates both about the axis of the central drive shaft 10, and its own axis which is perpendicular to 10. In this way, the axis of the cylinder would be perpendicular to the axis of 10.

When the substrates are loaded, the door of the chamber is closed, the chamber evacuated, and the gate valve opened to bring system pressure down to at least 10^{-5} to 10^{-6} Torr, which is the desired range of system base pressure. When the above base pressure is achieved, argon gas is introduced into the chamber via a needle valve or mass flow controller, until the chamber pressure reaches approximately 5×10^{-5} to 1×10^{-3} Torr, preferably about $1-3 \times 10^{-4}$ Torr. The filament current, the filament bias and the electromagnet power supply are then switched on. The filament current is the current that passes through the thermocathode (also called the filament or the cathode). The filament bias is the constant floating voltage applied to the filament (approximately -150V in relation to ground). Plasma current is measured as the current between the filament and the base plate or ground. This voltage provides the field that moves electrons emitted by the filament to the base plate 11. The electromagnet power supply provides current to the electromagnet, which creates a magnetic field that results in the electron path becoming a spiral, increasing the electron path length and improving the probability of collisions between the electrons and the vapor molecules created due to precursor evaporation.

- 17 -

The substrate bias power supply is concurrently switched on.

Switching on these power supplies results in
5 creation of an argon plasma, which is used to clean the
substrates prior to deposition. After the required
duration of cleaning, the precursor supply is opened.
Precursor flow is controlled via a needle valve and
occurs due to the difference in pressure between the
10 chamber and the outside atmosphere. When precursor flow
and vaporization in the chamber has stabilized, the argon
gas flow is turned off. The ionized precursor vapors
form a stable plasma, ions from which are accelerated
towards the substrate holder due to the substrate bias.
15 Thus, deposition of DLN film onto the substrate occurs.

Co-deposition of a dopant material is carried
out as follows. Argon flow to the magnetron is commenced
and the magnetron 8 is switched on after the base
20 pressure has been reached. A shutter 12 is used to
prevent deposition while the substrate is cleaned via
sputtering. When cleaning has been accomplished, the
shutter is opened and sputtering is carried out at the
desired power level. This may occur prior to commencement
25 of DLN film deposition, during DLN film deposition, after
DLN film deposition, or intermittently during DLN film
deposition, depending on what kind of film structure and
composition to be deposited are desired. Using DC or RF
sputtering, materials of all kinds (metals, ceramics,
30 alloys, etc.) can be used for co-deposition.

The growth conditions for nanocomposite films
are as follows, with reference to FIG. 2. The pressure
in the deposition chamber 1 should not exceed 10^{-3}
35 torr, with the pressure in the active zone of the plasma
generation 2, in the range from about 1.0×10^{-3} to about
 5.0×10^{-2} torr. The temperature of the substrate should

- 18 -

not exceed about 200°C with the temperature of the cathode filaments being in the range from about 2100 to about 2950°C. The current in the cathode filament is from about 70 to about 130 angstroms, with the voltage across the filament being from about 20 to about 30 V. The voltage with respect to the ground is from about 70 to about 130 V with the plasma current being from about 0.5 to about 20.0 angstroms. The voltage of the substrate holder is from about 0.1 to about 5.0 Kv, with all the carbon-containing and Si-containing species having kinetic energy in the range of from about 100 to about 1200 eV and from about 25 to about 300 eV respectively. The metal beams consist of free atoms or monatomic ions. The kinetic energy of the metal atoms/ions does not exceed from about 25eV. With a precursor flow rate from about 0.5 to about 5.0 cc/hour, the growth rate of the DLN is from about 0.1 to about 2.0 micrometers (microns)/hour.

For the powertrain component coatings of the present invention, the useful range of thickness is thought to be from about 0.1 to about 50 micrometers, more preferably from about 1 to about 10 micrometers, and is most preferably from about 2 to about 5 micrometers.

The preferred range of operation for most applications is a pressure of about $1-3 \times 10^{-4}$ Torr, a plasma current of about 1 amp., a filament current of from about 60 to about 75 amp., a substrate voltage of from about 600 to about 1000 V DC, or forward power of about 100 W in RF mode. The preferred frequency for RF mode is from about 90 to about 300 KHz. The preferred magnetron power depends on the type of material, composition and structure desired for the DLN coating.

In a further preferred embodiment, a preferred method of deposition uses a plasma discharge in a triode plasmatron, as shown schematically in FIG. 3, with the

- 19 -

plasma energy density above about 5 Kwh/gram-atom of carbon. The charged particles are extracted by a high voltage field in the vacuum chamber and directed onto the substrate 5. It is preferable that the potential of the substrate holder is from about -0.3 to about +5.0 Kv, and most preferably 1.0 +/- 0.2 Kv for DC and RF. In the RF mode, the frequency is in the range of from about 0 to about 25 Mhz for DC, and more preferably from about 90 to about 300 kHz for RF. The ratio of the electron emission to the carbon precursor flow in the plasmatron is from about 0.5 to about 1.5 electrons per particle.

Organosilicon compounds, such as siloxane, are preferred precursors for C, H, Si and O. One preferred organosilicon compound is polyphenylmethyilsiloxane, containing 1 to 10 Si atoms. The high boiling point siloxanes may be introduced directly into the active plasma region through a porous ceramic or metallo-ceramic (3 in FIGS. 3 and 4) which is heated via radiation thermocathodes 4. The photon and electron emission of the thermocathodes affect the evaporation, fragmentation and ionization of the precursor molecules on the surface of the ceramic, which thereby functions as an ion source for the plasma generator. An alternative method for injection of the siloxane precursors is to use direct injection from a diffusion pump.

The formation of dopant-containing beams may be realized by any one of, or combination of, the following methods: 1) thermal evaporation; 2) ion-sputtering; 3) ion beams. The dopant-containing beams are directed onto the growing film surface through the vacuum chamber to exclude interparticle collisions in the deposition chamber itself. Substrates are placed in an adjacent chamber on a rotating substrate holder, (for example a drum) which ensures double rotary motion, said adjacent chamber being connected to the plasma generation chamber

- 20 -

by an opening for the emission of the atomic or ionic beams, as shown schematically in FIG. 2. Alternatively, the plasma generation may be carried out within the chamber containing the substrates (FIG. 2). A DC or a
5 radio frequency potential is generally applied to the substrates during the deposition process. No external substrate heating is required. The substrate holder may be designed specifically to hold parts of different shapes such as cylinders, as would be apparent to one
10 skilled in the field.

Useful variation of the above described methods for deposition of DLN films include the use of sputtered silicon and oxygen gas as precursors for the Si and O₂,
15 the use of sputtered carbon and hydrogen or hydrocarbon gas used as carbon and hydrogen precursors, or any combination thereof.

For deposition on non-conducting substrates,
20 such as plastic, a method whereby a flow of neutral radicals is reflected from a high voltage target and directed to the substrate as shown schematically in FIG. 4. The process employs depositions similarly to those shown in FIG. 3, except that a reflecting electrode
25 is used to generate a neutral beam. This process eliminates surface damage of the substrate resulting from charged and/or fast particles impinging on the substrate during growth.

30 A preferred method for depositing thin undoped DLN films comprises ion bombardment (e.g. Ar⁺ or K⁺ with energy in the range of from about 30 to about 150 eV) through a vacuum chamber which has been backfilled by siloxane vapor (about 3×10^{-4} torr). This results in a
35 self-stabilized growth of a nanocomposite film, with the maximum thickness controlled by the maximum tunneling

- 21 -

distance for the relaxation of the charge of the absorbed radicals.

Therefore, the above-described flexible
5 coatings of the present invention may be deposited on the selected substrate in thicknesses ranging from a few nanometers to a few microns, preferably from about 20nm to about 12 micrometers, depending only on the desired application of the coated substrate. The deposition may
10 be tailored or "tuned" to meet the properties required for a particular application. The random interpenetrating of the two- or three-network DLNs guarantee uniform strength of the structures in all directions. The structures are free of micropores even
15 at thicknesses of 80 Angstroms (8 nm). The DLNs are therefore extremely stable and possess unique combinations of chemical, mechanical, electronic, and superconducting properties.

20 The following examples serve only to further illustrate aspects of the present invention and should not be construed as limiting the invention.

EXAMPLE 1

25

Coating of Samples with DLN

Square polished coupon samples of aluminum 6061 measuring 2"x2"x1/4" were coated with a three micron
30 thick Zr-DLN coating. Several coupons were cleaned with alcohol and mounted in the coating chamber on the substrate holder plate using metal clips. The chamber was closed and pumped down to 3×10^{-5} Torr. Argon gas flow was started and increased until the chamber pressure
35 reached 1.5×10^{-4} Torr. The magnetron shutter was closed and the magnetron power supply was switched on. Ion cleaning of the coupon began at a power level of 200 W.

- 22 -

After 20 minutes of cleaning, the filament current was turned on and increased to 65 amps while the filament bias voltage was -158 V and electromagnet current was 250 milliamps. Substrate RF bias was switched on to 100 W forward power at a frequency of 210 kHz. Substrate holder rotation was started and maintained at 7 rpm. After 10 minutes, of plasma cleaning of the substrate (coupon), the precursor needle valve was opened to a setting of 3 cc/hour. After about 5 minutes, the argon gas flow was stopped. A plasma current of about 1 amp was obtained. Concurrently, the magnetron shutter was opened to a setting of 450 W. Substrate load power was about 80 W. After about 4 hours, the precursor valve was closed, and the power supplies switched off. The chamber and substrates within were allowed to cool. The chamber was then backfilled with nitrogen and the DLN coated aluminum coupons removed from the substrate holder.

EXAMPLE 2

20 Wear-Resistance

Coated aluminum samples are prepared as described in Example 1, except that only a 2 micron thick layer of Zr-DLN is deposited. The coated samples are subjected to a pin on disk wear tester. The rounded tip of a steel pin having a 10mm diameter is placed against the DLN-coated sample surface. No lubricant is used and a force of 1 to 5 N is applied to the pin. The pin moves at a sliding velocity of 1 to 400 cm/s. The pin motion on the sample is either circular or reciprocal. Friction is measured continuously by means of transducers attached to the drive mechanism. Up to 200,000 cycles, the samples would show no wear.

- 23 -

EXAMPLE 3Thermal Stability of DLN Films

DLN films were tested for stability under high annealing temperatures, both in air and in vacuum. Thermal stability and maintained adhesion is required for the protection of weapon systems which undergo severe thermal shock and cycling under operating conditions. Annealing at 400°C in air for 9 hours followed by 600°C for 1 hour in vacuum did not change the film structure or degrade its properties. No film delamination was observed following the thermal testing that was carried out on DLN films. Analyses were carried out via visual observation, mechanical property determinations on annealed films and FTIR spectroscopy to determine changes in film structure. The values were found to deteriorate only approximately 10% after exposure to elevated temperatures of from about 400-500°C.

EXAMPLE 4Mechanical Properties of DLN Films - Hardness

High hardness and mechanical modulus measurements were obtained on 9 different compositions of DLN and doped-DLN films. Measurements were carried out using a nanoindenter (Nano instruments, Knoxville, TN) Hardness ranged from about 5 to about 21 GPa. Elastic modulus of approximately 60-220 GPa was achieved, which matches approximately the modulus of steel. Hardness/modulus degradation in the films was minimal after exposure to 500°C. The hardness of the doped and undoped DLNs were plotted as a function of compressive stress. Both the doped and undoped DLNs showed a material with higher hardness values for a given stress

than the sampled amorphous hard carbon (a DLC). See Figure 5.

5 Many other modifications and variations of the present invention are possible to the skilled practitioner in the field in light of the teachings herein. It is therefore understood that, within the scope of the claims, the present invention can be practiced other than as herein specifically described.

10

- 25 -

WHAT IS CLAIMED:

1. A method for inhibiting wear of a powertrain component comprising:
5 providing a powertrain component; and
applying to said component a coating made from a diamond-like solid state material formed from interpenetrating networks comprising a diamond-like carbon network stabilized by hydrogen, a silicon network
10 stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.
2. A method for reducing friction of a
15 powertrain component comprising:
providing adjacent powertrain components; and
applying to at least one of said powertrain components a coating made from a diamond-like solid state material formed from interpenetrating networks comprising
20 a diamond-like carbon network stabilized by hydrogen, a silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.
- 25 3. The method according to claim 1, wherein the carbon, hydrogen, silicon and oxygen are obtained from the decomposition of an organosiloxane having from about 1 to about 10 silicon atoms.
- 30 4. The method according to claim 3, wherein the organosiloxane is polyphenylmethyilsiloxane.
5. The method according to claim 1, wherein
35 the carbon content of the diamond-like solid state material is from about 40 wt.% to about 98 wt.%.

6. The method according to claim 1, wherein the carbon content of the diamond-like solid state material is from about 50 wt.% to about 98 wt.%.
- 5 7. The method according to claim 1, wherein the carbon to silicon weight ratio of the diamond-like solid state material is from about 2:1 to about 8:1.
- 10 8. The method according to claim 1, wherein the silicon to oxygen weight ratio of the diamond-like solid state material is from about 0.5:1 to about 3:1.
- 15 9. The method according to claim 1, wherein the dopant elements are selected from the group consisting of B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Mn, Ni, Ti, Zr, Cr, Re, Hf, Cu, Al, N, Ag, and Au.
- 20 10. The method according to claim 1, wherein the carbon content of the diamond-like solid state material is greater than about 40 atomic % of the DLN, the hydrogen content is up to about 40 atomic % of the carbon, and the sum of the silicon, oxygen and dopants together is greater than about 2 atomic % of the DLN.
- 25 11. The method according to claim 1, wherein the coating is deposited on the component to a thickness of from about 0.1 to about 50 micrometers.
- 30 12. A powertrain component in an internal combustion engine, the component comprising:
a substrate; and
a wear-resistant coating applied to said substrate, said coating made from a diamond-like solid
35 state material formed from interpenetrating networks comprising a diamond-like carbon network stabilized by hydrogen, a silicon network stabilized by oxygen, and

- 27 -

optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

- 5 13. The component according to claim 12, wherein the carbon, hydrogen, silicon and oxygen in the coating are obtained from the decomposition of an organosiloxane having from about 1 to about 10 silicon atoms.
- 10 14. The component according to claim 13, wherein the organosiloxane is polyphenylmethyilsiloxane.
- 15 15. The component according to claim 12, wherein the carbon content in the coating is from about 40 wt.% to about 98 wt.%.
- 20 16. The component according to claim 12, wherein the carbon content in the coating is from about 50 wt.% to about 98 wt.%.
- 25 17. The component according to claim 12, wherein the carbon to silicon weight ratio in the coating is from about 2:1 to about 8:1.
- 30 18. The component according to claim 12, wherein the silicon to oxygen weight ratio in the coating is from about 0.5:1 to about 3:1.
- 35 19. The component according to claim 12, wherein the dopant elements in the coating are selected from the group consisting of B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Mn, Ni, Ti, Zr, Cr, Re, Hf, Cu, Al, N, Ag, and Au.
20. The component according to claim 12, wherein the carbon content of the diamond-like solid

state material is greater than about 40 atomic % of the DLN, the hydrogen content is up to about 40 atomic % of the carbon, and the sum of the silicon, oxygen and dopants together is greater than about 2 atomic % of the
5 DLN.

21. The component according to claim 12, wherein the substrate comprises a material selected from the group consisting of metals, metal alloys, plastics
10 and ceramics.

22. The component according to claim 12, wherein the coating is deposited to a thickness of from about 0.1 to about 50 micrometers.

15 23. An internal combustion engine comprising a powertrain component coated with a wear-resistant coating formed from a diamond-like solid state material formed from interpenetrating networks comprising a diamond-like
20 carbon network stabilized by hydrogen, a silicon network stabilized by oxygen, and optionally at least one network made from dopant elements or dopant compounds containing elements from Groups 1-7b and 8 of the periodic table.

25 24. The engine according to claim 23, wherein the carbon, hydrogen, silicon and oxygen in the coating are obtained from the decomposition of an organosiloxane having from about 1 to about 10 silicon atoms.

30 25. The engine according to claim 24, wherein the organosiloxane is polyphenylmethysiloxane.

26. The engine according to claim 23, wherein the carbon content in the coating is from about 40 wt.%
35 to about 98 wt.%.

- 29 -

27. The engine according to claim 23, wherein the carbon content in the coating is from about 50 wt.% to about 98 wt.%

5 28. The engine according to claim 23, wherein the carbon to silicon weight ratio in the coating is from about 2:1 to about 8:1.

10 29. The engine according to claim 23, wherein the silicon to oxygen weight ratio in the coating is from about 0.5:1 to about 3:1.

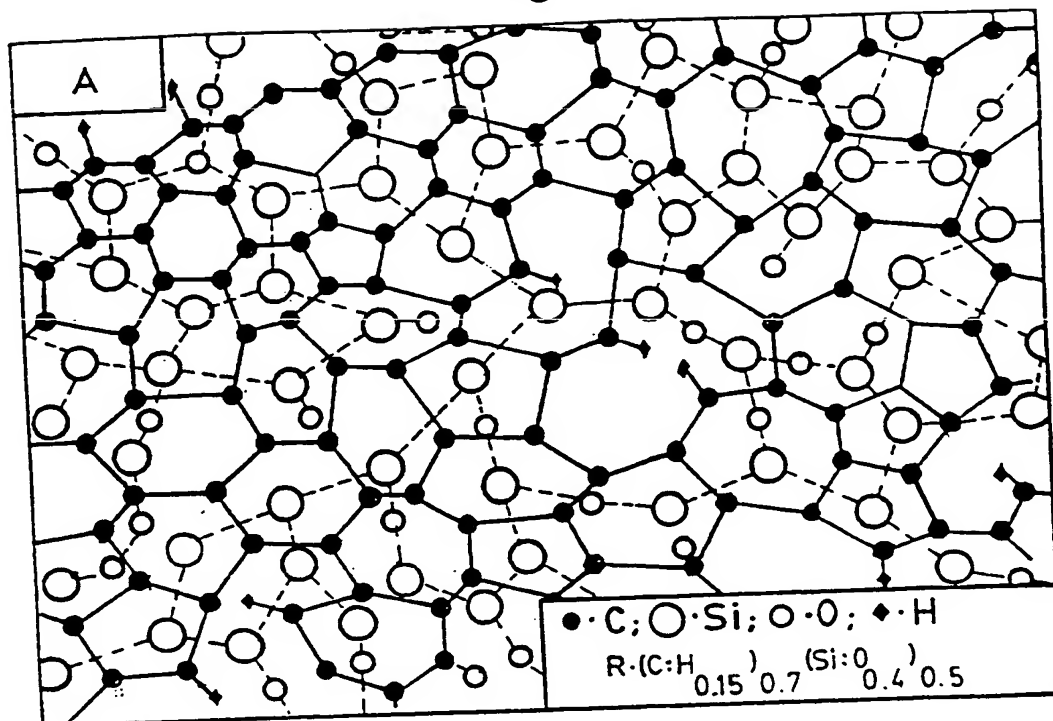
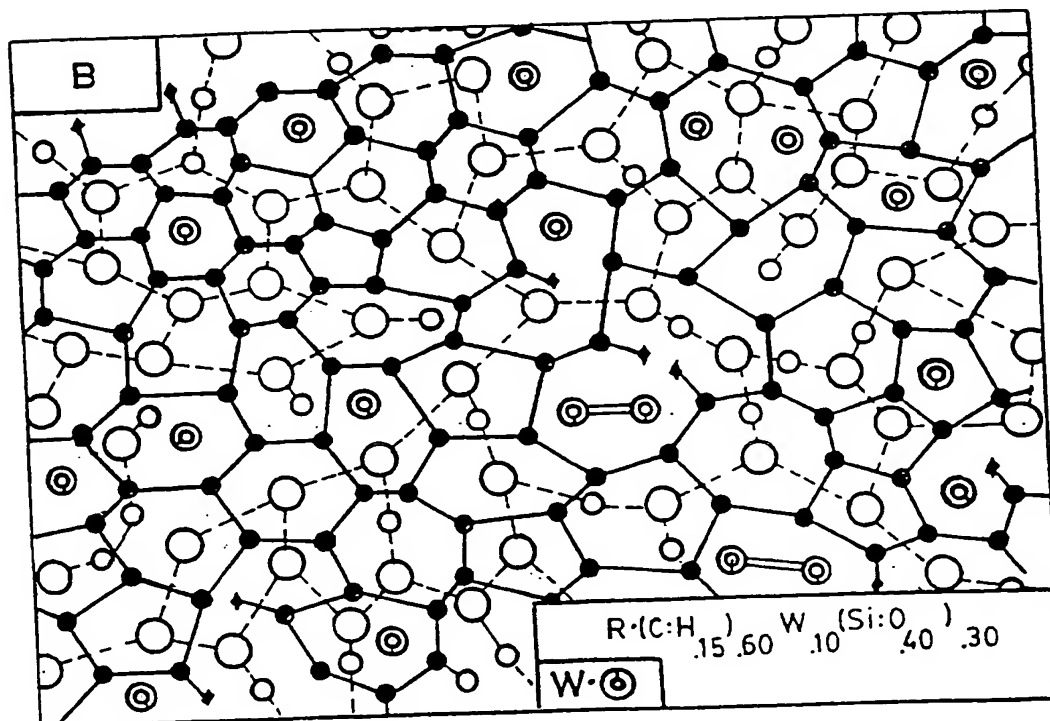
15 30. The engine according to claim 23, wherein the dopant elements in the coating are selected from the group consisting of B, Si, Ge, Te, O, Mo, W, Ta, Nb, Pd, Ir, Pt, V, Fe, Co, Mg, Mn, Ni, Ti, Zr, Cr, Re, Hf, Cu, Al, N, Ag, and Au.

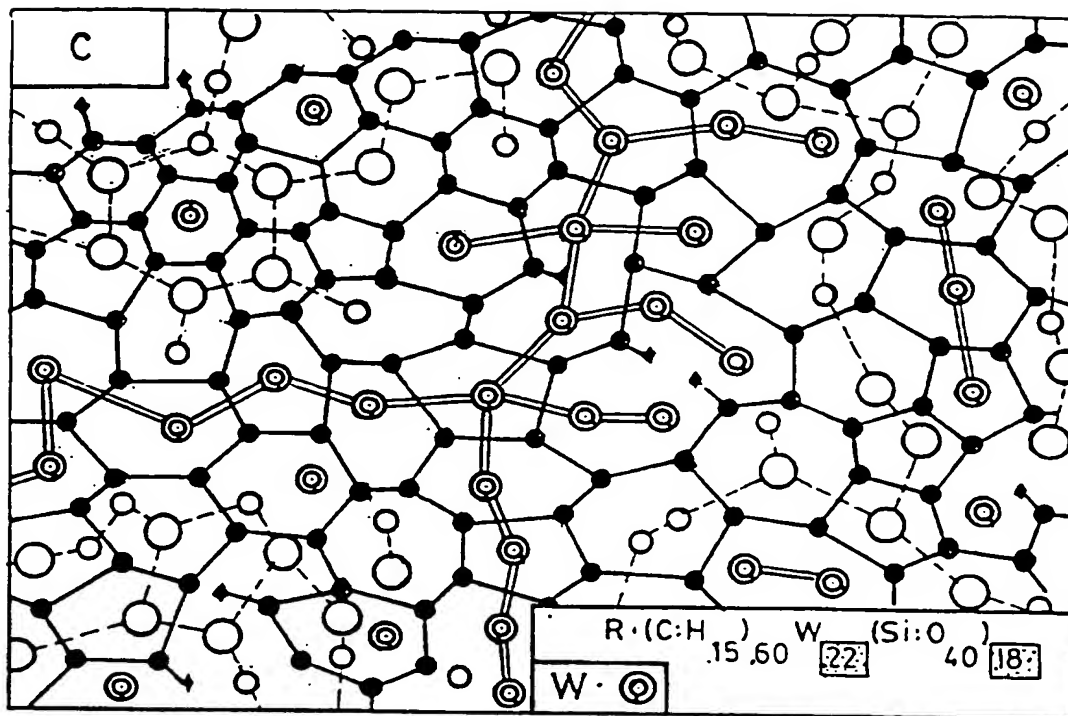
20 31. The engine according to claim 23, wherein the carbon content of the diamond-like solid state material is greater than about 40 atomic % of the DLN, the hydrogen content is up to about 40 atomic % of the carbon, and the sum of the silicon, oxygen and dopants together is greater than about 2 atomic % of the DLN.

25

32. The engine according to claim 23, wherein the coating is deposited to the component to a thickness of from about 0.1 to about 50 micrometers.

30

FIG. 1AFIG. 1B

FIG. 1C

3/6

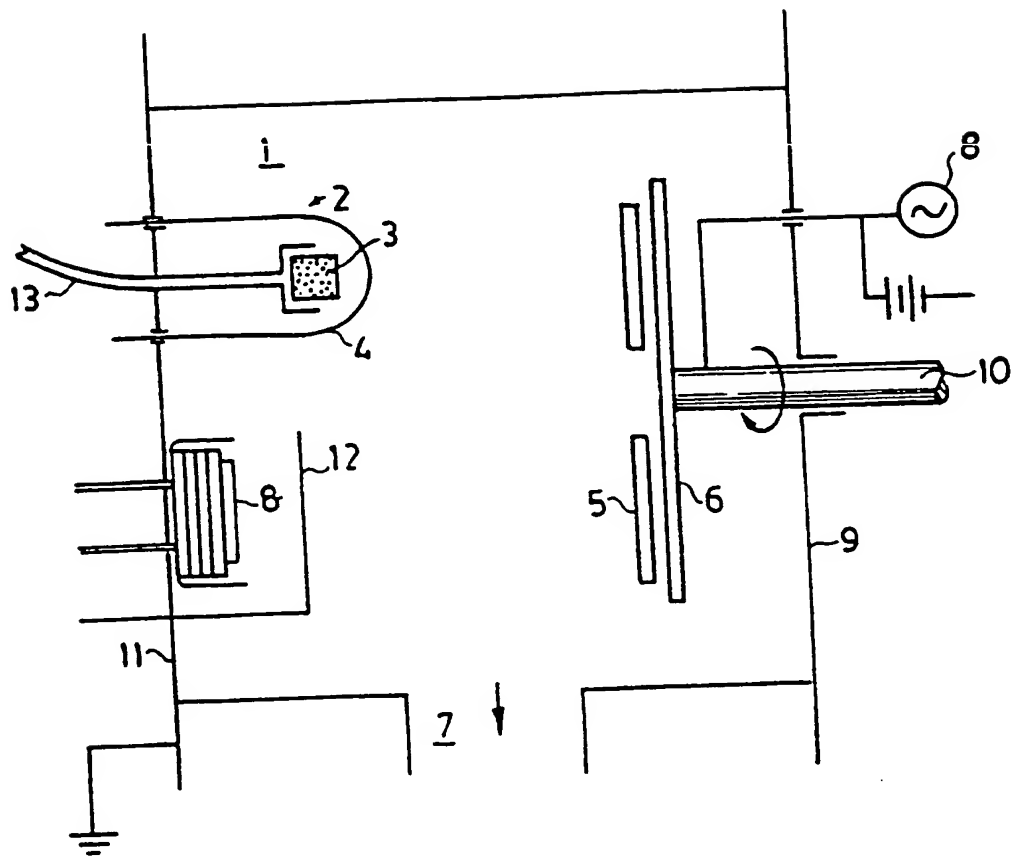
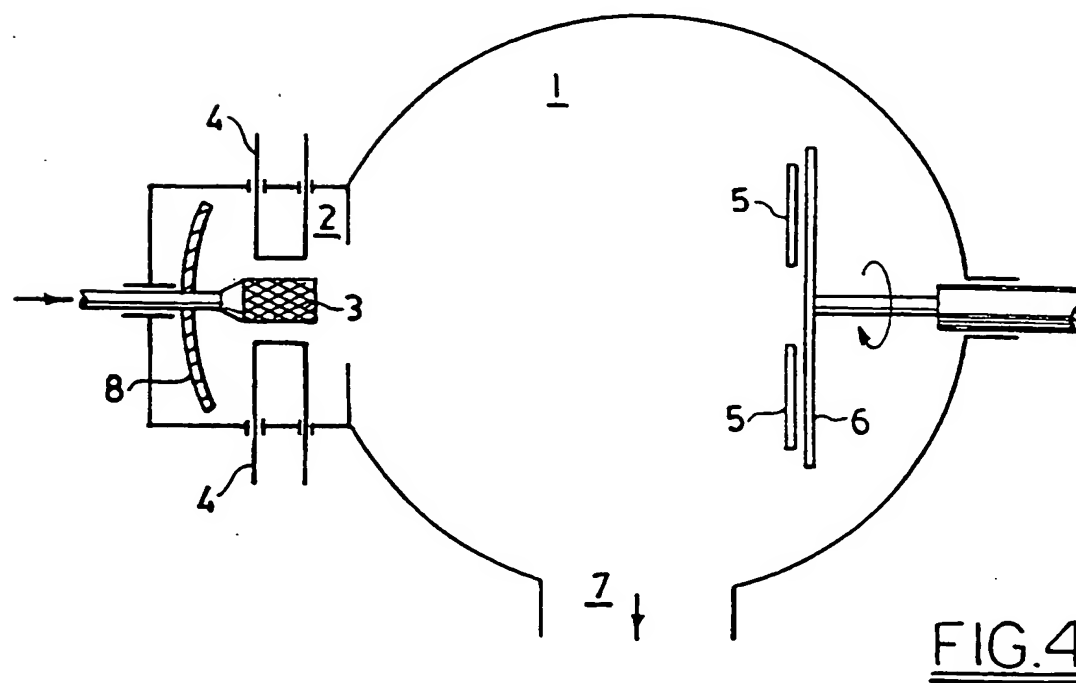
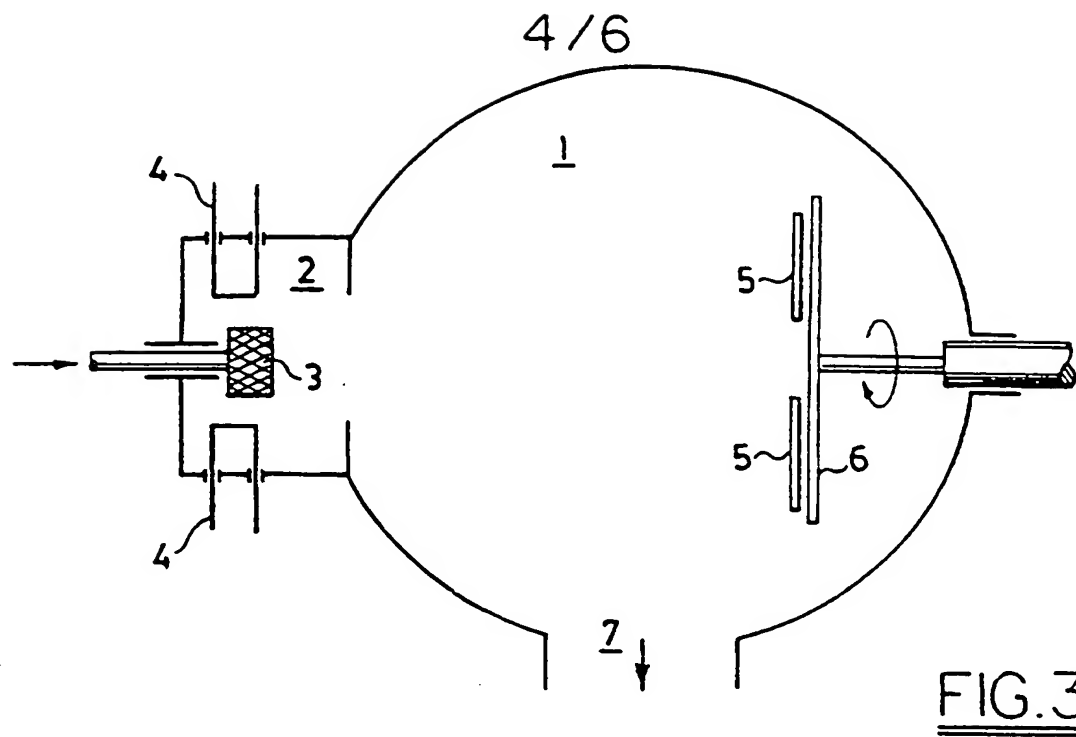


FIG.2

SUBSTITUTE SHEET (RULE 26)



5/6

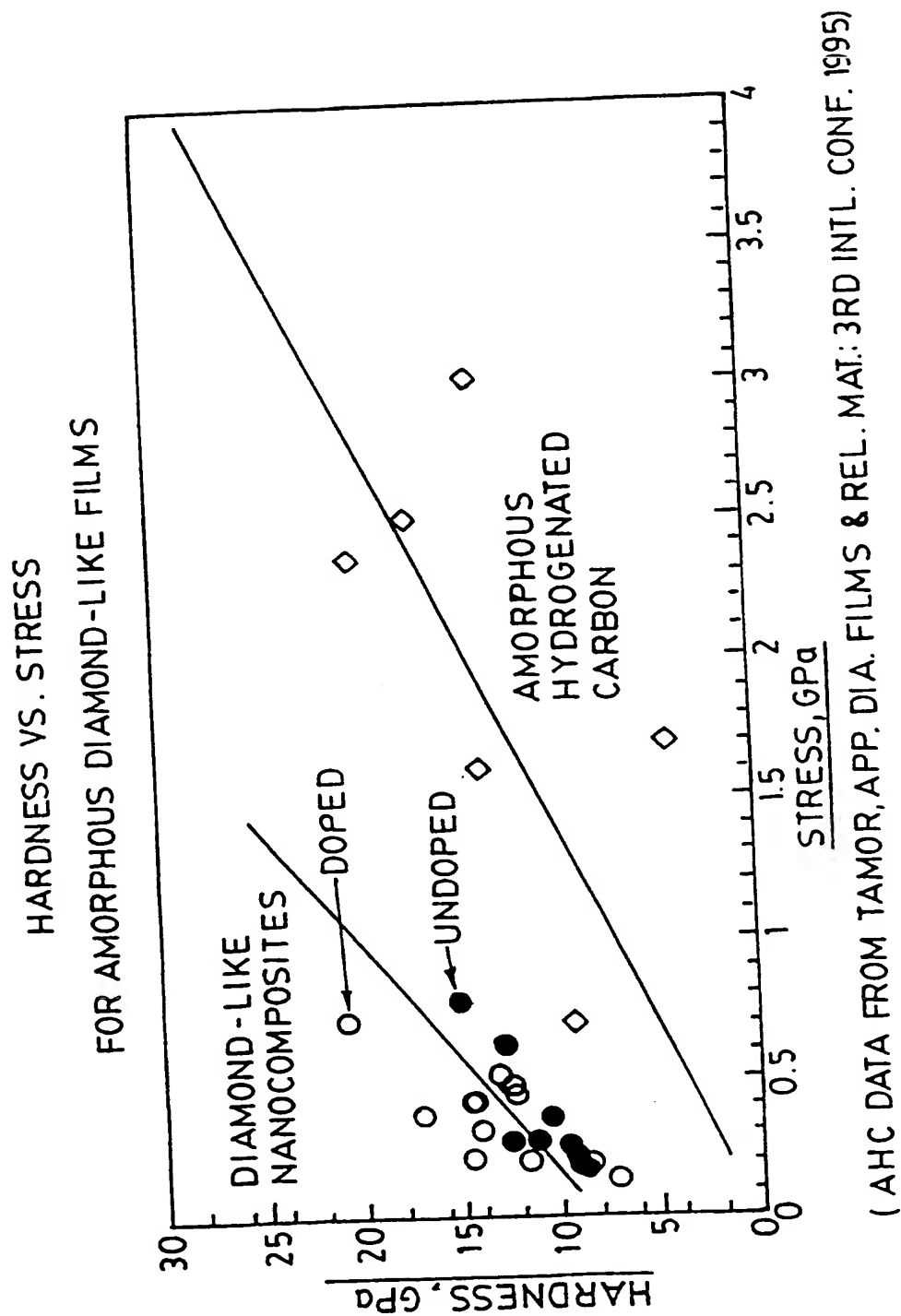


FIG. 5

SUBSTITUTE SHEET (RULE 26)

6/6

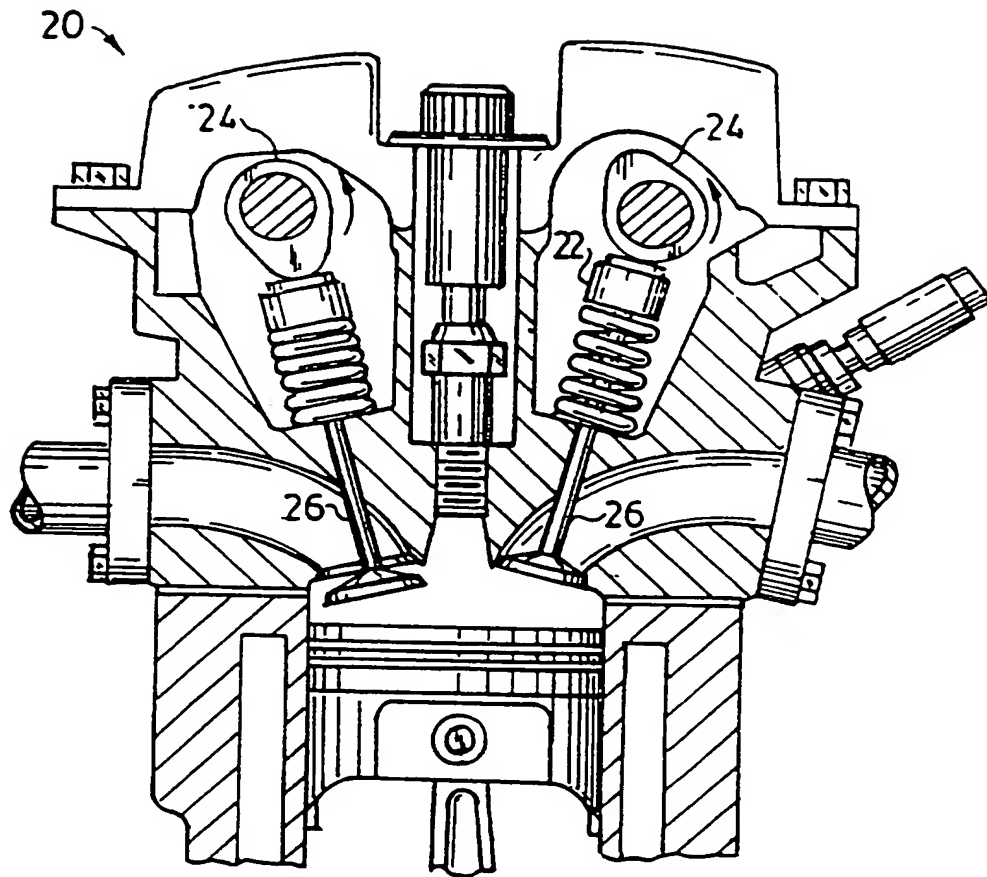


FIG. 6

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/15367

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 123/90.48, 90.51, 188.3, 668; 423/415.1, 445R, 446; 427/249; 428/336,408,446,469,697,704

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,237,967A (WILLERMET et al) 24 August 1993, abstract.	1-32
Y	US 5,352,493A (DORFMAN et al) 04 October 1994, col. 3, line 50-col.4 line 64.	1-32

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* L		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* (U)		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* &	document member of the same patent family

Date of the actual completion of the international search

09 JANUARY 1997

Date of mailing of the international search report

25 MAR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ARCHENE A. TURNER

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/15367

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

B32B 9/00, 9/04, 13/04, 15/04, 19/00; C01B 31/00, 31/02; C23C 16/00; F01L 1/44, 3/00, 3/04; F02B 75 /08, 77/02

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

123/90.48, 90.51, 188.3, 668; 423/415.1, 445R, 446; 427/249; 428/336,408,446,469,697,704

THIS PAGE BLANK (USPTO)